REPORT DOCUMENTATION PAGE

Form Approved OMB No. 074-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1997	From Proceeding of 1997 Workshop

4. TITLE AND SUBTITLE
Fundamental Limits on Gas-Phase Chemical Reduction of NOx in a Plasma

5. FUNDING NUMBERS
N/A

6. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
SERDP
901 North Stuart St. Suite 303
Arlington, VA 22203

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
N/A

11. SUPPLEMENTARY NOTES
This work was performed under the auspices of the US Department of Energy under contract number W-7405-ENG-48. From Proceedings of the 1997 Diesel Engine Emissions Reduction Workshop.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release: distribution is unlimited.

12b. DISTRIBUTION CODE
A

13. ABSTRACT ***(Maximum 200 Words)***

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14. SUBJECT TERMS
NOx; NO2; nitric acid; SERDP; SERDP Collection

15. NUMBER OF PAGES
6

16. PRICE CODE N/A

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclass.	unclass.	unclass.	UL

CP777

Proceedings of the 1997 Diesel Engine Emissions Reduction Workshop

FUNDAMENTAL LIMITS ON GAS-PHASE CHEMICAL REDUCTION OF NO_x IN A PLASMA

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Abstract: This paper examines the gas-phase chemical reduction of NO_x. It is shown that under the best conditions, the plasma can chemically reduce 1.6 grams of NO_x per brake-horsepower-hour when 5% of the engine output energy is delivered to the plasma. This NO_x reduction efficiency is a fundamental limit that cannot be exceeded in the absence of heterogeneous reactions or chemical additives. Higher NO_x removal efficiencies would suggest reactions of plasma oxidation products (such as NO_2 or nitric acid) on surfaces or particulates.

I. Introduction

In the plasma, the electrons do not react directly with the NO_x molecules. The electrons collide mainly with the background gas molecules like N_2, O_2 and H_2O. Electron impact on these molecules result partly in dissociation reactions that produce reactive species like N, O and OH. The dissociation of N_2 molecules produces N. The dissociation of O_2 produces O. The dissociation of H_2O produces OH. The N, O and OH species are the components of the plasma that eventually lead to the chemical conversion of NO_x. The NO_x in the engine exhaust gas initially consist mostly of NO. The ground state nitrogen atom, N, is the only species that could lead to the chemical reduction of NO to N_2. The O radical oxidizes NO to NO_2, leaving the same amount of NO_x. The OH radical converts NO_2 to nitric acid. Acid products in the plasma can easily get adsorbed on surfaces in the plasma reactor and in the pipes. When undetected, the absence of these oxidation products can often be mistaken for chemical reduction of NO_x.

Whether the electrons in the plasma dissociate N_2 or O_2 depends on the speed of the electrons. Slow electrons are more likely to dissociate O_2 and produce oxidizing radicals. Very fast electrons are required to dissociate N_2. The probability for dissociation of N_2 has a maximum value that cannot be exceeded regardless of the plasma reactor design or other components in the exhaust gas. It is a fundamental limit dictated by the known physics of electron-molecule collisions.

In this paper we will examine the gas-phase chemical reduction of NO_x. We will show that under the best conditions, the plasma can chemically reduce 1.6 grams of NO_x per brake-horsepower-hour [$g(NO_x)$/bhp-hr] when 5% of the engine output energy is delivered to the plasma.

II. Units

The unit of electron volts (eV) is used to express both the electron kinetic energy and the electrical energy consumption. The electron kinetic energy is a measure of the speed of an electron. For example, an electron with a 1 eV kinetic energy has a speed of 5.9×10^5 m/s, that is, 0.2% the speed of light. On the other hand, an electrical energy cost of 1 eV per NO_x molecule corresponds to the usage of 7.8×10^{-4} bhp-hr/$g(NO_x)$. The mass of NO_2 is used here to represent NO_x. For example, suppose the plasma requires an electrical energy consumption of 40 eV to remove one NO_x molecule. If the plasma uses 5% of the engine energy output, then the amount of NO_x that can be removed is $[0.05 / (40 \times 7.8 \times 10^{-4})] = 1.6$ $g(NO_x)$/bhp-hr.

Another unit commonly used to express the NO_x conversion efficiency in the plasma is the electrical energy density, given in units of Joules per liter (J/L). It is equal to the power delivered to the plasma divided by the exhaust gas flow rate. An engine with a load of 100 kW and an exhaust gas flow rate of 7600 liters per minute (L/min) has an energy density output of (10^5 J/s) / ((127 L/s) = 790 J/L. For example, suppose a plasma reactor consumes 20 J/L to remove 100 ppm of NO_x. This means that the plasma reactor will consume 100 x (20 J/L) / (790 J/L) = 2.5% of the engine energy output to remove that 100 ppm of NO_x.

III. Electron Kinetic Energy

The intent in using a non-thermal plasma is to selectively convert the input electrical energy to the kinetic energy of the electrons. An ideal situation would be where the kinetic energy of the electrons is dissipated entirely in the dissociation of NO molecules. However, because of the relatively low concentration of NO in the exhaust gas, direct dissociation of NO by the electrons is not probable. The kinetic energy of the electrons is deposited primarily into the major exhaust gas components, N_2 and O_2.

The physics of electron collisions with the N_2 and O_2 molecules determines the electrical energy cost for the NO_x conversion chemistry. The chemistry in the plasma always start with electron-impact dissociation of the abundant molecules. The efficiency for dissociation of various molecules is determined by the average kinetic energy of the electrons. The average electron kinetic energy is determined by the electron-molecule collision cross section and the electric field experienced by the electrons.

The electrons could lose considerable kinetic energy through reactions, such as the vibrational excitation of N_2, which heats up the N_2 molecule but does not promote the conversion of NO_x. The most useful deposition of electron kinetic energy into N_2 and O_2 is associated with the production of N and O radicals through electron-impact dissociation:

$$e + N_2 \rightarrow e + N(^4S) + N(^4S,^2D) \quad (1)$$

$$e + O_2 \rightarrow e + O(^3P) + O(^3P,^1D) \quad (2)$$

where $N(^4S)$ and $N(^2D)$ are ground-state and metastable excited-state nitrogen atoms, respectively, and $O(^3P)$ and $O(^1D)$ are ground-state and metastable excited-state oxygen atoms, respectively.

The NO_x in the engine exhaust gas initially consist mostly of NO. The ground state atomic nitrogen, $N(^4S)$, is the only species produced by the plasma that can lead to the gas-phase chemical reduction of NO:

$$N(^4S) + NO \rightarrow N_2 + O \quad (3)$$

The gas-phase chemical reduction of NO_x is therefore determined by the electron-impact dissociation of N_2.

IV. Collision Cross Section

The electron-molecule collision cross section represents the probability that the molecule will undergo a specific reaction (for example, dissociation) when hit by an electron. The collision cross section is expressed in units of a geometrical cross sectional area, typically on the order of 10^{16} cm^2. If the electron hits a circular target of this size perpendicular to its path and centered at the molecule, then the reaction occurs. If it misses that area, then the reaction does not occur.

The collision cross section is a fundamental quantity that has been measured by atomic physicists. The cross section for electron collision with a particular molecule is independent of the composition of the exhaust gas. The cross section for electron-impact dissociation of N_2 has a maximum that cannot be exceeded regardless of the plasma reactor design or the way the electrical voltage is delivered to the plasma reactor.

Figure 1 shows the cross section for electron impact on N_2 leading to neutral atomic nitrogen products [1].

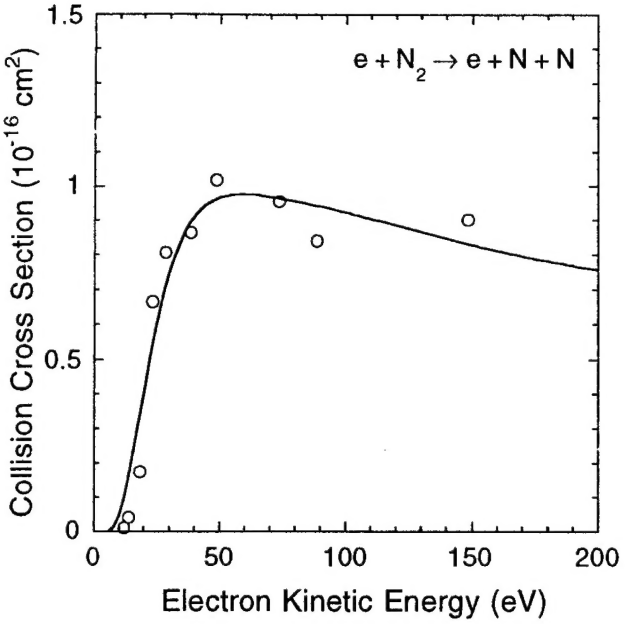

Figure 1. Cross section for electron-impact dissociation of N_2.

V. Electric Field

There are basically only two types of non-thermal plasma reactors: discharge and electron beam. Discharge plasma reactors are those reactors in which the high voltage electrodes are immersed in the atmospheric-pressure gas stream. The attainable electron kinetic energy in this kind of reactor is very limited. The electrons collide rapidly with the background gas molecules and therefore cannot be accelerated to very high kinetic energies. Electron beam plasma reactors are those reactors in which the high voltage electrodes are in vacuum. The electrons are accelerated in the vacuum region before they are injected into the exhaust gas stream.

The electric field in a discharge plasma is determined largely by the electrical breakdown threshold. Under atmospheric-pressure conditions, the electric field experienced by the discharge plasma is between 30 and 60 kV/cm [2], as shown in Figure 2.

Because of the limited range of electric fields that the electrons experience inside a discharge plasma, the average kinetic energy that the electrons can attain is also very limited.

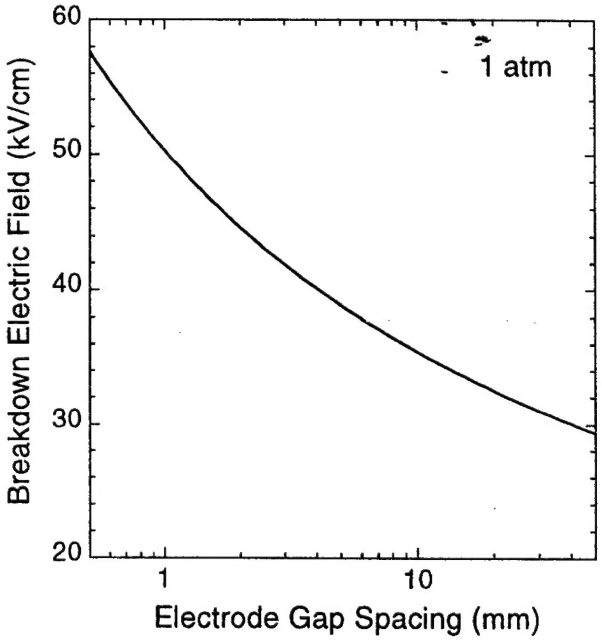

Figure 2. Breakdown electric field in an atmospheric-pressure discharge plasma.

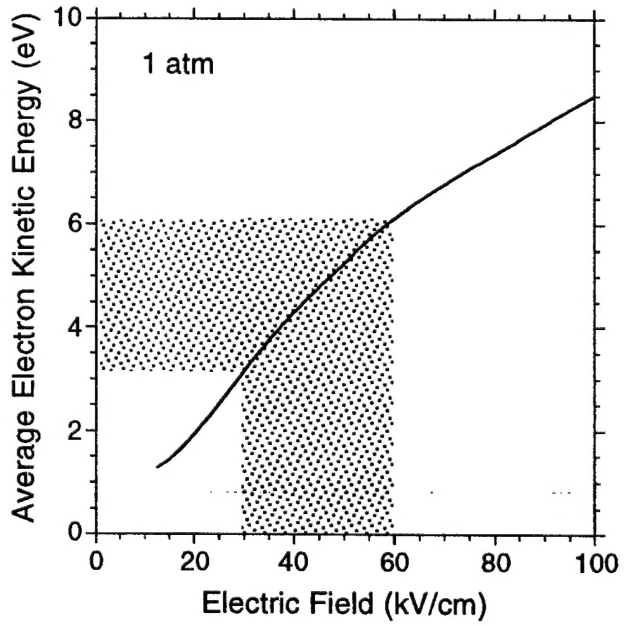

Figure 3. Average electron kinetic energy as a function of the electric field in an atmospheric-pressure discharge plasma.

Figure 3 shows the average electron kinetic energy as a function of the electric field. All discharge plasma reactors have average electron kinetic energies of 3 to 6 eV [3].

VI. Electrical Energy Cost

For now let us assume an ideal condition in which the plasma is not producing oxidative radicals. Let us further assume that all nitrogen atoms (labeled simply as N) are used entirely for the reduction of NO:

$$N + NO \rightarrow N_2 + O \qquad (4)$$

In this case the electrical energy required to reduce NO is simply determined by the electrical energy required to produce N from the electron-impact dissociation of N_2. What is the energy required to implement this reduction scheme?

The electrical energy cost for the dissociation of N_2 is proportional to the average electron speed and inversely proportional to the dissociation rate. The average electron speed, known as the electron drift velocity, is a balance between energy gain because of electron acceleration by the electric field and energy loss because of electron collisions with the molecules. Like the average kinetic energy, the drift velocity is determined by the electron-molecule collision cross sections and the electric field.

To minimize the electrical energy cost, one would like to have the highest dissociation rate. The dissociation rate is proportional to the dissociation cross section. The rate for dissociation of N_2 has a maximum because of the maximum in the cross section for electron-impact dissociation of N_2. The minimum electrical energy consumption for dissociation is determined by the maximum rate for dissociation.

The electrical energy cost can be expressed as a function of the electric field or the average kinetic energy of the electrons in the plasma. Figure 4 shows the electrical energy cost for N atom production as a function of the average electron kinetic energy. The electrical energy cost for NO_x reduction by reaction (4) is equal to that for N atom production.

The electrical energy cost is very sensitive to the speed of the electrons. For most discharge plasma reactors the average electron kinetic energy is 4 eV [3]. In this case the electrical energy cost for NO_x reduction is around 240 eV per NO_x molecule. This means that if the plasma uses 5% of the engine energy output, then the amount of NO_x that can be removed is [0.05 / (240 x 7.8×10^{-4})] = 0.27 g(NO_x)/bhp-hr. To remove 2 g(NO_x)/bhp-hr, the plasma would need at least 37% of the engine's output energy!

Fast electrons are required to minimize the electrical energy cost for NO_x reduction. There are many proposals on how the electron kinetic energy can be increased. For the sake of establishing a fundamental limit, let us assume that a very high electron kinetic energy can be achieved in practice. As shown in Figure 4, the minimum electrical energy cost is 40 eV per NO_x molecule [4]. Under this condition, the plasma can chemically reduce 1.6 g(NO_x)/bhp-hr when 5% of the engine output energy is delivered to the plasma.

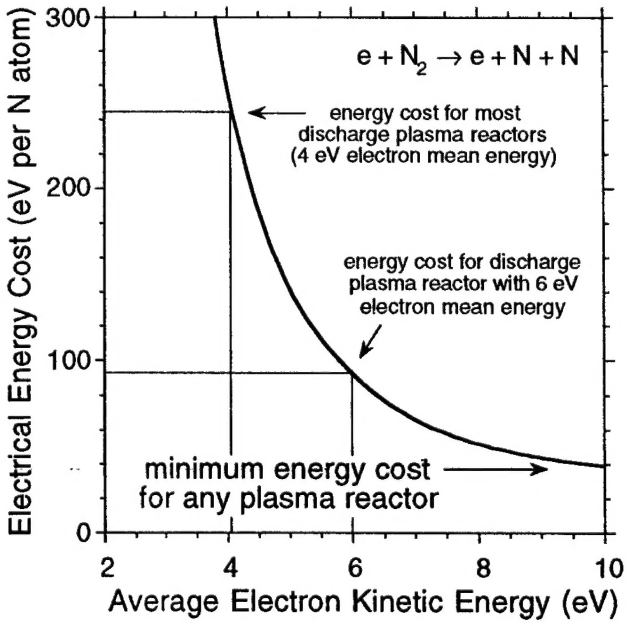

Figure 4. Electrical energy cost for N atom production as a function of the average electron kinetic energy.

Figure 5 shows the conversion between eV per NO_x molecule to g(NO_x)/bhp-hr. The curves correspond to different percents of engine output energy applied to the plasma.

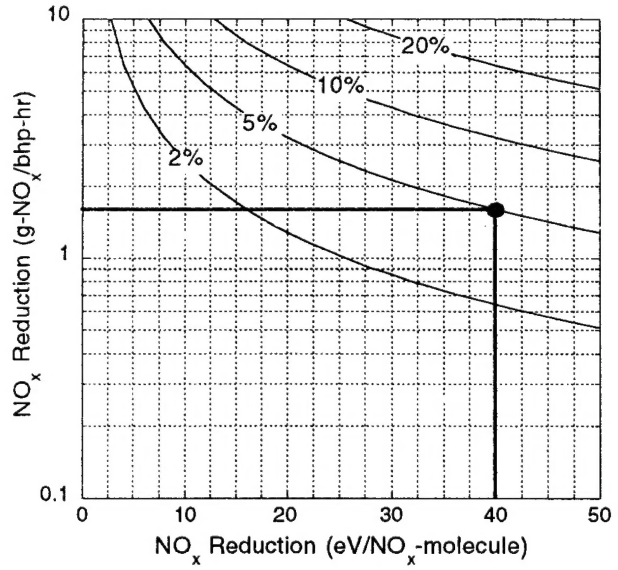

Figure 5. Conversion curves between eV per NO_x molecule to g(NO_x)/bhp-hr. The curves correspond to different percents of engine output energy applied to the plasma. The value of 40 eV per NO_x molecule is the minimum electrical energy cost for gas-phase chemical reduction of NO_x in a plasma. This energy cost corresponds to a maximum NO_x reduction of 1.6 g(NO_x)/bhp-hr when 5% of the engine output energy is applied to the plasma.

VII. Effect of Oxygen

It is much easier and cheaper for the electrons to dissociate O_2 compared to N_2. The dissociation of O_2 will produce only oxidative radicals. With O_2 concentrations of 5% or more, a significant fraction of the electrical energy delivered to the plasma is dissipated in the dissociation of O_2. The ground state oxygen atoms, $O(^3P)$, convert NO to NO_2:

$$O(^3P) + NO + M \rightarrow NO_2 + M \quad (5)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (6a)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (6b)$$

Reactions (5) and (6) convert NO to NO_2 and leaves the same amount of NO_x.

During the dissociation of O_2, a significant fraction of the atomic oxygen products is in the excited state. This metastable excited-state atomic oxygen, $O(^1D)$, reacts with H_2O to produce OH radicals. The OH radicals convert NO and NO_2 to nitrous acid and nitric acid, respectively. Acid products in the plasma can easily get adsorbed on surfaces in the plasma reactor and in the pipes. When undetected, the absence of these oxidation products are often mistaken for chemical reduction of NO_x.

In the presence of O_2, not all of the N atoms resulting from the dissociation of N_2 lead to the reduction of NO. Dissociative excitation of N_2 contributes a large fraction to the total N_2 dissociation [5]. A significant species produced by dissociative excitation of N_2 is the long-lived metastable, $N(^2D)$. For fast electrons, over half of the total N atoms produced are in the excited metastable states. The rate constants characterizing the interaction of the metastable species $N(^2D)$ with various gases are large [6]. In the treatment of NO, there are two competing reactions involving the $N(^2D)$ metastable species:

$$N(^2D) + NO \rightarrow N_2 + O \quad (7)$$

$$N(^2D) + O_2 \rightarrow NO + O \quad (8)$$

With 500 ppm NO and 10% O_2, the $N(^2D)$ species is twenty times more likely to react with O_2 than with NO. This means that $N(^2D)$ is consumed in the production of NO rather than in the reduction of NO. Whereas the reaction of ground state N atoms, $N(^4S)$, with O_2 can proceed only at very high temperatures, the reaction of excited N atoms, $N(^2D)$, with O_2 can proceed even at room temperature. Since almost half of the total N atoms produced in the plasma are in this excited state, the reduction of NO by the ground state N atoms is almost completely counterbalanced by the production of NO by the excited N atoms. What is left in terms of NO_x conversion chemistry is the oxidation of NO to NO_2.

VIII. Heterogeneous Reactions

What we have examined in this paper is the gas-phase chemical reduction of NO_x. Heterogeneous reactions in the plasma reactor can also take place. Absorption of NO_2 and nitric acid on particulates and reactor walls is often mistaken for gas-phase chemical reduction. There may be conditions in which one can take advantage of plasma oxidation products as intermediaries for the heterogeneous chemical reduction of NO_x.

IX. Conclusions

The gas-phase chemical reduction of NO_x in a plasma can be accomplished via reaction with atomic nitrogen. Under the best condition, the plasma can chemically reduce 1.6 grams of NO_x per brake-horsepower-hour when 5% of the engine output energy is delivered to the plasma. This NO_x reduction efficiency is a fundamental limit that cannot be exceeded in the absence of heterogeneous reactions or chemical additives.

Fast electrons are required to optimize the production of atomic nitrogen from electron-impact dissociation of N_2. Unfortunately, a large fraction of the atomic nitrogen produced by the fast electrons are in the excited state. In the presence of O_2, the excited-state nitrogen atoms lead to the production of NO. Thus the development of plasma reactors that can produce fast electrons is not the key to achieving high NO_x reduction efficiency when O_2 is present in the exhaust gas.

With the O_2 concentrations present in diesel and lean-burn engine exhausts, the dissociation of O_2 is the most dominant dissociation reaction that takes place in the plasma. The dissociation of O_2 promotes the gas-phase oxidation of NO to NO_2 and nitric acid, but not the gas-phase reduction of NO_x to N_2. Absorption of NO_2 and nitric acid on particulates and reactor walls is often mistaken for gas-phase chemical reduction of NO_x.

X. Acknowledgments

This work was performed at Lawrence Livermore National Laboratory under the auspices of the U.S. Department of Energy under Contract Number W-7405-ENG-48, with support from the Chemical Sciences Division of the Office of Basic Energy Sciences and a Cooperative Research and Development Agreement with Cummins Engine Company.

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